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The structural and electrical characterization of a $HfErO_x$ dielectric for MIM capacitor DRAM applications

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ABSTRACT

Hafnium erbium oxide ($HfErO_x$) thin films were formed using atomic layer deposition. The effect of using different Hf:Er pulse ratios on the electrical and structural properties of the $HfErO_x$ thin films (~9 nm) in metal–insulator–metal (MIM) capacitor structures have been investigated and comparisons made between as-deposited and annealed samples. We report the stabilisation of the higher dielectric constant (*k*) tetragonal/cubic phase by optimising the Hf:Er pulse ratio. The dielectric properties post thermal anneal at 500 °C were studied. A leakage current in the order of $\sim 1 \times 10^{-8}$ (A/cm^2) at a voltage of 1 V and a capacitance equivalent thickness of ~1.4 nm have been achieved post thermal annealing at 500 °C.

1. Introduction

Metal–insulator–metal (MIM) capacitors play an essential role in dynamic random access memory (DRAM) and logic applications [1,2]. With the on-going scaling of the minimum device dimensions of logic and memory devices, the choice of the dielectric incorporated into these MIM capacitors is critical [3]. Currently, the semiconductor roadmap requires film properties to be superior to those of silicon nitride in two distinct areas. First, the leakage current must be in the order of 10^{-8} A/cm^2 and secondly a capacitance equivalent thickness (CET) in the sub-nanometer range is required. To achieve these demanding dielectric targets high dielectric constant (high-*k*) thin films must be used, and an increasing amount of research activity is now focussed on the integration of different high-*k* materials to achieve the target values for optimum dielectric constant and leakage current density [3,4].

Hafnium oxide (HfO_2) is now used as a gate dielectric [5] for logic CMOS due to its high dielectric constant, chemical and thermal stability and the resulting low gate current leakage. Erbium is a rare earth element which has been used in laser applications because of its optical properties but has found only limited use in semiconductor devices [6] as well as MOS structures [7]. It has been shown that doping HfO_2 with rare earth elements can reduce the leakage current and increase the *k* value in metal insulator silicon (MIS) capacitors [8]. High-*k* films have been deposited on silicon substrates using physical vapour deposition (PVD) [9] but recently Weimer et al. have fabricated MIS structures with Er doped (~15%) HfO_2 thin films using atomic layer deposition (ALD) [10]. In this paper we examine Er doped HfO_2 films containing a range of different Hf to Er ratios deposited by ALD and incorporated into MIM structures for potential DRAM applications. Structural characterization of the $HfErO_x$ films have been performed using transmission electron microscopy (TEM) and X-ray diffraction (XRD). Capacitance–voltage and current–voltage analysis have been used to electrically access the different $HfErO_x$ MIM structures.

2. Experimental and sample details

The MIM layers were deposited onto an *n*-type Si (100) wafer with *n*+ type As surface doping ($\sim 5 \times 10^{19}$ cm^{-3}). TiN (10 nm) was deposited by metal organic chemical vapour deposition (MOCVD) and $HfErO_x$ films of varying Hf:Er pulse ratios were deposited

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by ALD in a ASM Pulsar® 2000, hot wall cross flow reactor, at a deposition temperature of 325 °C using bis(methylcyclopentadienyl)methoxymethyl hafnium (HfD-04, SAFC Hitech), tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium, ($Er(thd)_3$, SAFC Hitech), and Ozone as precursors. The samples were formed with nominal Hf:Er pulse ratios of 1:1, 4:1 and 8:1. The samples were given a Rapid Thermal Anneal (RTA) in a Jipelec Jetfirst 150 system for 60 s in N_2 (1000-mbar pressure) at 500 °C. Blanket un-annealed and annealed samples were used for comparative physical measurements. Test structures were then fabricated to replicate a DRAM MIM capacitor structure using a lithography and lift off process, with a range of top metal areas from 400 μm^2 to 1.6×10^5 μm^2. The top metal electrode consisted of Ti (10 nm) and Al (200 nm) formed in sequence using e-beam deposition. The metals used to form the upper and lower electrodes are all CMOS compatible and meet current industrial standards [11].

Samples for TEM examination were made using the H-bar technique [12] and milled to electron transparency in an FEI 200 workstation. Final milling was performed at a beam current of 11 pA. The samples were examined at 200 eV using a range of microstructural characterization techniques in a JEOL2010. The XRD system used was PANalytical X'Pert Pro MPD X-ray diffractometer with CuK_α radiation. 1° incident angle and detector scan mode was used for the running conditions. Current–voltage (I–V) and capacitance–voltage (C–V) measurements were carried out using a HP4156B precision semiconductor parameter analyser and a HP4284A precision LCR meter, respectively. All electrical measurements were taken from a wafer at 25 °C in a micro-chamber probe station (Cascade Micro-tech model Summit 12561B) in a dry air environment.

3. Experimental results

3.1. TEM analysis

TEM was used to assess the layer microstructure and the thickness of the as-deposited samples. Fig. 1(a–c) shows typical regions of the capacitor structure for which the Hf:Er pulsing ratios were 1:1, 4:1 and 8:1, respectively. The 25 nm amorphous oxide formed below the TiN electrode was found to be heavily As doped and to be characteristically inhomogeneous containing a number of different sub-layers consistent with the locally variable As doping. The TiN bottom electrode, which was found to be similarly irregular, had a low density band at its center whilst exhibiting the formation of more localised regions that extend into the underlying As doped oxide to depths of up to 18 nm. The as-deposited $HfErO_x$ layers were found to be crystalline, in agreement with Böscke et al. [13] who made similar observations for HfO_2 films deposited at thicknesses greater than 7 nm. The thickness and grain size of the $HfErO_x$ layers are shown in Table 1 as a function of the Hf:Er pulsing ratios. As the Er concentration is reduced, the thickness of the dielectric layer remain almost constant but the grain size increases as is evident in Fig. 1. Table 1 also shows that the grain size of the $HfErO_x$ increases upon annealing. Given that the layer thickness of the $HfErO_x$ films are constant as a function of the Hf:Er pulsing ratio, within experimental limitations, any significant capacitance changes can be attributed to changes in the k value of the dielectric.

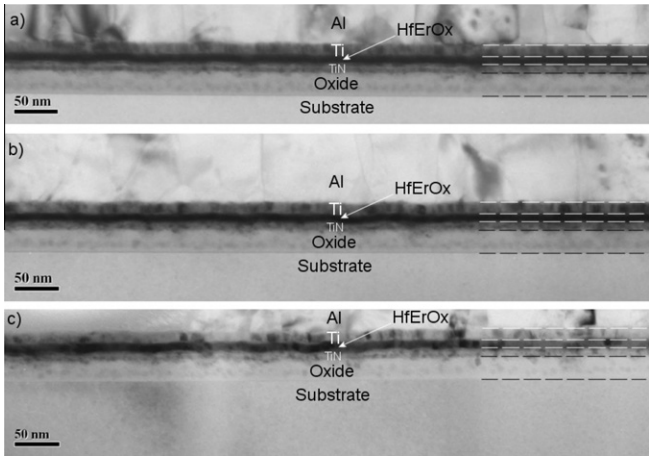

Fig. 1. Bright field TEM micrograph of the as-deposited structures with Hf:Er pulse ratios of (a) 1:1, (b) 4:1 and (c) 8:1.

3.2. XRD analysis

The XRD data for the as-deposited samples are shown in Fig. 2 for which there are a number of differences as a function of the Hf:Er layer concentration. The 8:1 Hf:Er samples exhibit two distinct peaks corresponding to the monoclinic HfO_2 phase at 2θ 28.5° and the tetragonal/cubic HfO_2 phase at 2θ 30.5° [13]. The 1:1 Hf:Er and 4:1 samples by comparison show only one peak, at 2θ 30.5° thus indicating that the monoclinic phase formation has been suppressed with increasing erbium concentration. The addition of erbium also led to a slight shift of the diffraction peak at 2θ 30.5° towards the (222) plane of the Er_2O_3 cubic phase at 2θ 29.5° [14]. This shift of the cubic/tetragonal peak seen in the 1:1 sample could be due to the large erbium content resulting in the presence of the cubic phase of pure Er_2O_3. The presence of cubic Er_2O_3 phase within the dielectric could explain the lower k value of the 1:1 sample compared with the 4:1 sample. Moreover, the monoclinic phase was not detected in the Hf:Er 1:1 sample yet the measured capacitance was comparable to the Hf:Er 8:1. As the Er_2O_3 content in HfO_2 is increased, the $HfErO_x$ film k value will be reduced as the contribution of the pure ErO_2 (k of $Er_2O_3 \sim 12$–14) to the overall film dielectric constant will be more significant.

3.3. Electrical characterization

Fig. 2 shows the C–V response for the $HfErO_x$ MIM structure with a Hf:Er pulsing ratio of 8:1 following an RTA anneal (area = 1×10^4 μm^2) at 500 °C. The measurement frequency was ranged from 1 kHz to 1 MHz and the oscillation level was 0.05 V. The capacitance was measured using both the Cs–V (series) and Cp–V (parallel) modes, and Fig. 3 illustrates the effect of the AC signal frequency and the equivalent circuit mode.

Before discussing the multi-frequency capacitance voltage (C–V) response, it is important to note the difference observed between the C–V characteristics in the series and the parallel modes. A perfect capacitor will yield identical C–V characteristics irrespective of the mode employed. However, when the measured capacitor presents resistive components due to resistance in series or leakage through the dielectric, this will cause divergence of the two measurement modes. When measured in Cp–V mode, a capacitor with a significant series resistance component will exhibit a strong dispersion with the measurement frequency i.e. the mea-

Table 1
Grain size and layer thickness measurements of the as-deposited and annealed $HfErO_x$ films formed with different pulsing ratios.

Hf:Er pulse ratio	Condition	Grain size (nm)	Thickness (nm) (±0.5 nm)
1:1	As deposited	5–7	9
4:1	As deposited	5–10	9
	500 °C Anneal	20	8.5
8:1	As deposited	6–15	9
	500 °C Anneal	15–25	9.5